

Comparison of Different *Ab Initio* Theoretical Models for Calculating Isodesmic Reaction Energies for Small Ring and Related Compounds

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ABSTRACT

Isodesmic reactions are commonly used in *ab initio* studies to partially cancel errors associated with incomplete basis sets and incomplete correction for electron correlation. The errors associated with these reactions have been examined using the 6-31G* basis set at the theoretical levels HF, MP2, MP3, MP4, and B3LYP, and using the 6-311 + G* basis set at the HF, MP2, and B3LYP levels. As a comparison, the recently developed model chemistries, CBS-4 and CBS-Q, were also used. With hydrogenation and hydrogenolysis reactions, only the HF level gave large deviations from the experimental reaction energies. The use of hydrogen transfer reactions improved the HF calculated energies, but mixed results were obtained at the correlated levels. Some isomerization reactions and reactions of carbocations also were examined. The MP4/6-31G* and CBS-Q levels of theory were uniformly the more satisfactory. © 1997 by John Wiley & Sons, Inc.

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Introduction

All *ab initio* theoretical models contain some approximations such as the use of incomplete basis sets and incomplete correction for electron correlation.¹ The errors associated with these approximations often cancel when isodesmic reactions are considered. We were interested in seeing how well the approximations did cancel in examining some reactions involving small ring compounds. Therefore, we have calculated the energies of a series of compounds having three- and four-membered rings along with some unstrained compounds. Geometry optimizations were carried out at the HF/6-31G*, MP2(full)/6-31G*, MP2(full)/6-311 + G*, B3LYP/6-31G*, and B3LYP/6-311 + G* levels. The latter is a density functional theory model² that has been successful in studying several chemical problems.³ Both the MP2 and B3LYP methods correct for electron correlation, although via different procedures. Frozen

core MP3 and MP4 calculations were carried out using the MP2/6-31G* geometries. The zero-point energies were calculated at the HF/6-31G* level and scaled by 0.893.⁴

In addition, two model chemistries, recently developed by Ochterski et al.,⁵ CBS-4 and CBS-Q, also were used. The less computationally intensive of the two models is CBS-4, which is practical for up to 12 nonhydrogen atoms. This model starts with a HF/3-21G* geometry, then uses a large basis set HF calculation (6-311 + G(3d2f, 2df, p)). This notation is a simple extension of standard basis set notation to indicate there is an extra *d* and *f* function on elements sodium through argon. The CBS extrapolation is applied to an MP2/6-31 + G^{††} calculation. Here, the dagger (†) symbol indicates that the polarization functions have been taken from the 6-311G** basis set. Finally, the authors use an MP4(SDQ)/6-31G calculation to approximate higher than second order effects. This model also has corrections for zero-point energy and spin contamination and a size-consistent, higher-order correction.

TABLE I.
Calculated Energies, 6-31G*.

Compound	ZPE ^a	HF	MP2	MP3	MP4	B3LYP
Hydrogen	5.9	-1.12683	-1.14414	-1.14933	-1.15093	-1.17548
Methane	26.8	-40.19517	-40.33704	-40.34862	-40.35479	-40.51839
Ethyne	16.5	-76.81783	-77.07622	-77.07588	-77.09356	-77.32565
Ethene	30.7	-78.03172	-78.29429	-78.30597	-78.31980	-78.58746
Ethane	44.7	-79.22876	-79.50397	-79.52090	-79.53281	-79.83042
Propyne	33.7	-115.86432	-116.25624	-116.25961	-116.28406	-116.65327
Propene	47.9	-117.07147	-117.46966	-117.48566	-117.50562	-117.90756
Propane	61.9	-118.26365	-118.67441	-118.69606	-119.71404	-119.14425
Butane	79.1	-157.29841	-157.84497	-157.87127	-157.89542	-158.45804
Isobutane	78.2	-157.29898	-157.84777	-157.87335	-157.89784	-158.45881
Allene	33.3	-115.86110	-116.24852	-116.25854	-116.28076	-116.65767
1,3-Butadiene	51.3	-154.91965	-155.44171	-155.45565	-155.48433	-155.99214
Cyclopropene	33.9	-115.82305	-116.21957	-116.22607	-116.24707	-116.61904
Cyclopropane	48.9	-117.05887	-117.46283	-117.47683	-117.49477	-117.89520
Cyclobutane	66.7	-156.09720	-156.63706	-156.65584	-156.68054	-157.21315
Cyclohexane	102.2	-234.20801	-235.02161	-235.04845	-235.08582	-235.88043
Bicyclo[1.1.0]butane	52.2	-154.87177	-155.40948	-155.41770	-155.44381	-155.94805
Bicyclo[1.1.1]pentane	70.7	-193.90568	-194.58233	-194.59330	-194.62756	-195.26056
[1.1.1]propellane	50.3	-192.69107	-193.37471	-193.37043	-193.41089	-194.00898
Benzene	60.3	-230.70314	-231.48719	-231.48624	-231.53175	-232.24865
Isopropyl cation	53.2	-117.38116	-117.76065	-117.78156	-117.79972	-118.21183
<i>t</i> -Butyl cation	69.6	-156.44241	-156.95954	-156.98492	-157.00929	-157.55420
Cyclobutyl cation	59.1	-155.22381	-155.74766	-155.76030	-155.78647	-156.29406
Cyclopropylcarbinyl cation	58.9	-155.22778	-155.74472	-155.75830	-155.78588	-156.29645
Bicyclo[1.1.1]pentyl-1 cation	61.6	-193.04241	-193.70207	-193.70807	-193.74384	-194.35175

^aBased on HF/6-31G* frequencies scaled by 0.893.

The CBS-Q model uses larger basis sets at every level of theory, and is practical for systems with up to six nonhydrogen atoms. Equilibrium geometries are calculated at the MP2(FC)/6-31G[†] level, while the CBS extrapolation is based on a MP2/6-311 + + G(3d2f, 2df, 2p) calculation. Higher-order contributions are estimated with two calculations: MP4(SDQ)/6-31 + G(d(f), d, p), where the "(f)" indicates that there are *f* polarization functions on the elements phosphorus through argon; and QCISD(T)/6-31 + G[†]. Again, this model has corrections for zero-point energy, spin contamination, and higher-order effects.⁵ In a study of model chemistries making use of comparison of 89 experimental and calculated heats of formation, the CBS-4 model gave a root-mean-square (rms) deviation of 2.1 kcal/mol, and CBS-Q gave a deviation of 1.1 kcal/mol.⁶ This may be compared with the computationally more demanding G2 model developed by Curtiss et al.,⁴ which also gave an rms deviation of 1.1 kcal/mol.

The sets of calculated energies are given in Tables I and II. In calculating the energy changes,

the HF, MP, and B3LYP energies must be corrected for the zero-point energies. These corrections are incorporated into the CBS-4 and CBS-Q energies. The observed energy changes are derived from the experimental heats of formation of 0 K (Table III).

Hydrogenation and Hydrogenolysis Reactions

The reactions of organic compounds with hydrogen to give reduction of C—C bonds or hydrogenolysis of C—C bonds are among the simplest of organic reactions. They are not isodesmic reactions in that the bond types are not the same between the reactants and products, and electron correlation effects for H—H and C—H bonds might well be different.⁷ We were interested in seeing how large the errors might be.

The energy changes are given in Table IV along with the average deviation and the rms deviation

TABLE II.
Calculated Energies, Extended Basis Sets.

Compound	6-311 + G*			CBS-4	CBS-Q
	HF	MP2	B3LYP		
Hydrogen	−1.12804	−1.14588	−1.17663	−1.17193	−1.16609
Methane	−40.20276	−40.36792	−40.52808	−40.42821	−40.40954
Ethyne	−76.83672	−77.13418	−77.35056	−77.19763	−77.18650
Ethene	−78.83672	−78.35337	−78.60836	−78.43839	−78.41575
Ethane	−79.24305	−79.56346	−79.84841	−79.66119	−79.62977
Propyne	−115.89013	−116.34287	−116.68561	−116.44971	−116.42256
Propene	−117.09497	−117.55741	−117.93619	−117.68073	−117.64511
Propane	−118.28476	−118.76298	−119.17052	−118.89877	−118.85471
Butane	−157.32635	−157.96255	−158.49248	−158.13701	−158.08071
Isobutne	−157.32705	−157.96602	−158.49338	−158.14017	−158.08349
Allene	−115.8856	−116.33442	−116.68799	−116.44776	−116.42307
1,3-Butadiene	−154.95141	−155.55663	−156.03028	−155.70560	−155.66569
Cyclopropene	−115.84475	−116.30325	−116.64605	−116.41323	−116.38187
Cyclopropane	−117.07868	−117.54906	−117.92100	−117.67369	−117.63117
Cyclobutane	−156.12369	−156.75203	−157.24612	−156.90985	−156.85831
Cyclohexane	−234.24842	−234.24769	−235.92981	−235.42815	−235.35099
Bicyclo[1.1.0]butane	−154.89839	−155.52234	−155.98095	−155.67012	−155.62153
Bicyclo[1.1.1]pentane	−193.93806	−194.72385	−194.29906	−194.90918	−194.84905
[1.1.1]Propellane	−192.72696	−193.51523	−194.04947	−193.67922	−193.62627
Benzene	−230.74600	−231.65307	−232.30070	−231.84743	−231.78886
Isopropyl cation	−117.40226	−117.84299	−118.23375	−117.96014	−117.92549
<i>t</i> -Butyl cation	−156.47013	−157.07027	−157.58358	−157.22697	−157.17918
Cyclobutyl cation	−155.24968	−155.85521	−155.32130	−155.98816	−155.94729
Cyclopropylcarbiny cation	−155.25380	−155.85230	−155.32516	−155.99002	−155.94757
Bicyclo[1.1.1]pentyl-1 cation	−193.07335	−193.83458	−194.38451	−193.99193	−193.94662

TABLE III.
Experimental Heats of Formation^a.

Compound	ΔH_f (298 K)	ΔH_f (0 K)
Methane	-17.8 ± 0.1	-15.9
Ethane	-20.0 ± 0.1	-16.3
Propane	-25.0 ± 0.1	-19.7
Butane	-30.0 ± 0.2	-23.5
Isobutane	-32.1 ± 0.2	-25.3
Cyclopropane	12.7 ± 0.1	16.9
Cyclobutane	6.6 ± 0.3	12.4
Cyclohexane	-29.5 ± 0.2	-20.1
Bicyclo[1.1.0]butane	51.9 ± 0.2	56.0
[1.1.1]Propellane	84 ± 1	88
Ethene	12.5 ± 0.1	14.5
Propene	4.8 ± 0.2	8.4
Allene	45.5 ± 0.3	47.3
Butadiene	26.3 ± 0.2	29.8
Cyclopropene	66.2 ± 0.6	67.4
Ethyne	54.5 ± 0.2	54.6
Propyne	44.2 ± 0.2	45.9
Benzene	19.7 ± 0.2	23.9

^aThe 298 K data were taken from J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, Vol. 1, Thermodynamics Research Center, College Station, TX 77843-3111. They were converted to 0 K using the scaled HF/6-31G* vibrational frequencies.

with respect to the experimental data. If the errors were randomly distributed, the average deviation would be close to zero. This is the case for larger basis set calculations that include electron correlation, and for the smaller basis set MP2 and MP4 calculations. The rms deviations from the experimental energies are, as expected, largest for the HF calculations. All of the MP methods gave generally small deviations, and it was quite small (2 kcal/mol) for MP4/6-31G*. The B3LYP/6-31G* energies led to larger deviations, especially for the reduction of acetylenes. Eliminating these two reactions would reduce the rms deviation to 2.6 kcal/mol. The B3LYP/6-311 + G* calculations eliminated this problem and led to a small rms error. For most of these reactions, B3LYP is as effective as MP2, and is generally computationally more economical.

The CBS-4 and CBS-Q calculations are on a different level than the others, involving the use of much larger basis sets and higher levels for electron correlation. The CBS-4 model leads to the same rms deviation as MP4, and the CBS-Q model gives remarkably good agreement with the experimental data.

TABLE IV.
Hydrogenation and Hydrogenolysis Reactions (kcal / mol).

Reaction ^a	Calculated heat of reaction, 0 K										
	6-31G*					6-311 + G*					Obs., 0 K
	HF	MP2	MP3	MP4	B3LYP	HF	MP2	B3LYP	CBS4	CBSQ	
$\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	-36.0	-33.0	-33.1	-30.9	-34.2	-33.5	-32.2	-31.7	-31.9	-30.1	-30.8 ± 0.1
$\text{H}_2\text{C}=\text{CHCH}_3 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8$	-32.9	-29.9	-30.2	-28.0	-30.3	-30.6	-29.4	-28.1	-28.9	-27.3	-28.1 ± 0.2
$\text{HC}\equiv\text{CCH}_3 + 2\text{H}_2 \rightarrow \text{C}_3\text{H}_8$	-82.3	-71.1	-75.4	-69.8	-80.1	-77.9	-69.9	-74.3	-75.1	-69.7	-73.0 ± 0.2
$\text{CH}_3\text{C}\equiv\text{CH} + 2\text{H}_2 \rightarrow \text{C}_3\text{H}_8$	-70.5	-65.1	-70.1	-64.0	-71.5	-70.5	-64.1	-66.2	-66.0	-62.7	-65.6 ± 0.2
$(\text{CH}_2=\text{CH})_2 + 2\text{H}_2 \rightarrow \text{C}_4\text{H}_{10}$	-62.5	-56.2	-57.4	-52.5	-56.1	-58.6	-55.6	-52.4	-54.9	-52.0	-53.3 ± 0.3
$c\text{-C}_3\text{H}_4 + \text{H}_2 \rightarrow c\text{-C}_3\text{H}_6$	-59.3	-53.1	-54.5	-51.6	-54.1	-57.3	-53.6	-52.6	-55.6	-52.2	-50.5 ± 0.1
$\text{C}_6\text{H}_6 + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_{12}$	-53.8	-39.8	-47.5	-39.4	-41.9	-50.0	-41.1	-38.1	-40.7	-40.1	-44.0 ± 0.3
$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	-18.8	-13.3	-13.9	-13.2	-16.4	-18.6	-10.4	-16.5	-14.6	-14.6	-15.5 ± 0.1
$\text{C}_3\text{H}_8 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_4$	-17.3	-10.4	-11.4	-10.5	-14.5	-17.0	-10.4	-14.7	-11.7	-11.6	-12.5 ± 0.2
$(\text{CH}_3)_3\text{CH} + \text{H}_2 \rightarrow \text{C}_3\text{H}_8 + \text{CH}_4$	-16.1	-7.7	-9.2	-8.0	-13.2	-15.8	-7.3	-13.3	-9.3	-9.2	-10.3 ± 0.2
$c\text{-C}_3\text{H}_6 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8$	-41.8	-35.2	-36.8	-35.8	-39.1	-41.9	-35.6	-38.6	-33.4	-36.1	-36.6 ± 0.1
$c\text{-C}_4\text{H}_8 + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10}$	-40.3	-33.5	-35.0	-33.6	-37.1	-40.3	-34.1	-37.3	-34.7	-35.3	-35.9 ± 0.4
$\text{bcButane} + \text{H}_2 \rightarrow c\text{-C}_4\text{H}_8$	-53.2	-43.8	-47.1	-45.2	-47.6	-52.4	-44.0	-47.0	-42.5	-44.4	-43.6 ± 0.4
$[1.1.1]\text{Propellane} + \text{H}_2 \rightarrow \text{bc}[1.1.1]\text{C}_5$	-40.6	-25.3	-31.6	-26.8	-33.3	-36.6	-24.9	-31.3	-36.4	-35.6	NA
Rms deviation	6.9	2.3	2.8	2.1	3.5	5.2	2.5	2.4	2.1	1.8	
Average deviation	-6.5	0.6	-1.7	1.3	-2.8	-5.0	0.9	-0.9	0.1	1.1	

^aThe prefix "c" indicates cyclo-,bc[1.1.1]C₅ is bicyclo[1.1.1]pentane.

Hydrogen Transfer Reactions

An alternative to the hydrogenation reaction is an isodesmic⁸ hydrogen transfer reaction of the type:



6-31G* basis:	HF	3.8	MP2	3.2
6-311 + G* basis:	HF	2.5	MP2	2.8
Other basis:	CBS-4	2.4	CBS-Q	1.5

Now, the deviation for the HF model is markedly reduced and, surprisingly, the errors for the MP2, MP3, and B3LYP/6-311 + G* models are significantly increased. The deviations for the B3LYP/6-31G*, CBS-4, and CBS-Q models are essentially unchanged.

The errors associated with these reactions depend on the error for the base reaction (i.e., in the hydrogenolysis of ethane). It can be seen in Table IV that this error is significant for MP2, MP3, and MP4. As a result, these methods give less satisfactory estimated energies for the hydrogen transfer reactions. It is clear that each component of an isodesmic reaction must be examined to see if satisfactory results can be obtained with a given level of theory.

Isomerization Reactions

Isomerization reactions generally lead to changes in bond types, and also might be expected

The two types of reactions are related by the hydrogenolysis energy of ethane given in Table III. The energies have considerable differences among theoretical models, and therefore there will be significant changes in deviations from experimental data. The rms deviations (kcal/mol) for the hydrogen transfer reactions are:

MP3	4.6	MP4	2.3	B3LYP	3.2
B3LYP	3.3				

to lead to less satisfactory cancellation of correlation errors. This is explored in Table V. In this limited group of reactions, MP4 and CBS-Q give relatively low deviations, whereas both B3LYP/6-31G* and CBS-4 give unusually large deviations. The main problem with the latter is found in the isomerization of benzene to three acetylenes. However, the use of the larger basis set with B3LYP led to a much improved heat of isomerization of benzene.

Reactions of Carbocations

The experimental data for the heats of formation of carbocations usually show relatively large experimental errors (~ 3 kcal/mol), and data are not available for many interesting carbocations. Nevertheless, it was of interest to compare the results obtained at the different levels of theory (Table VI).

TABLE V. Isomerization Reactions.

Reaction	Calculated heat of reaction, 0 K										
	6-31G*					6-311 + G*					Obs. (0 K)
	HF	MP2	MP3	MP4	B3LYP	HF	MP2	B3LYP	CBS4	CBSQ	
c-C ₃ H ₆ → CH ₃ CH=CH ₂	-8.9	-5.3	-6.5	-7.8	-8.8	-11.2	-6.2	-10.5	-4.4	-8.7	-8.5 ± 0.2
c-C ₃ H ₄ → CH ₃ C≡CH	-26.1	-23.2	-21.2	-23.4	-21.7	-28.7	-25.1	-25.0	-22.9	-25.5	-21.5 ± 0.6
c-C ₄ H ₈ → 2 H ₂ C=CH ₂	15.8	25.1	22.2	20.4	18.7	11.2	23.1	13.1	20.8	16.8	16.6 ± 0.3
bcbutane → (CH ₂ =CH) ₂	-20.9	-21.1	-24.7	-26.3	-28.6	-34.2	-22.4	-31.9	-22.3	-27.7	-26.2 ± 0.3
C ₆ H ₆ → 3 HC≡CH	145.9	151.4	151.5	146.7	159.7	137.2	146.4	145.5	159.7	143.9	146.2 ± 0.4
n-butane → isobutane	-1.3	-2.7	-2.2	-2.4	-1.4	-1.3	-3.1	-1.5	-2.0	-1.7	-1.8 ± 0.3
Allene → propyne	-1.6	-4.4	-0.3	-1.7	3.2	-2.4	-4.9	1.9	-1.2	0.3	-1.4 ± 0.3
Rms deviation	2.5	4.6	3.1	1.7	5.4	5.8	3.6	3.0	5.8	1.9	
Average deviation	-1.5	2.3	2.2	0.3	2.5	4.7	0.6	-1.7	3.5	-1.3	

TABLE VI.
Reactions of Carbocations.

Reaction	Calculated heat of reaction, 0 K										Obs. (0 K)
	6-31G*					6-311 + G*					
	HF	MP2	MP3	MP4	B3LYP	HF	MP2	B3LYP	CBS4	CBSQ	
2-Pr ⁺ + isobutane → <i>t</i> -Bu ⁺ + propane	-16.2	-15.9	-16.3	-16.1	-17.4	-16.0	-15.1	-16.8	-16.0	-15.6	-18.9 ± 3.0
c-C ₄ H ₇ ⁺ isobutane → <i>t</i> -Bu ⁺ + c-C ₄ H ₈	-11.4	-1.7	-5.5	-4.5	-10.1	-11.7	-1.7	-10.4	-5.3	-4.2	NA
bc[111] ⁺ + isobutane → <i>t</i> -Bu ⁺ + bc[111]	-3.7	5.5	2.5	3.5	-2.1	-4.4	4.6	-2.5	-2.5	1.2	~ 1 ± 1
c-C ₄ H ₇ ⁺ → c-C ₃ H ₅ CH ₂ ⁺	-2.7	1.6	1.1	0.2	-1.7	-2.8	1.6	-2.6	-1.2	-0.2	~ 0

^ac-C₄H₇⁺ is the cyclobutyl cation; bc[111]⁺ is the bicyclo[1.1.1]pentyl-1 cation; bc[1.1.1] is bicyclo[1.1.1]pentane; c-C₃H₅CH₂⁺ is the cyclopropylcarbinyl cation.

The hydride transfer from isobutane to the 2-propyl cation leads to approximately the same estimated energy change for all theoretical levels, and the values agree with the experimental data within the uncertainty of the latter. The hydride transfer from isobutane to the cyclobutyl cation gives a spread of calculated values where HF and B3LYP predict much more exothermic reactions than the other methods. The MP3, MP4, CBS-4, and CBS-Q methods all give essentially the same result, and it is probably correct.

The hydride transfer from isobutane to the bicyclo[1.1.1]pentyl-1 cation leads to a range of calculated energies having both positive and negative signs. The relative reactivity of bicyclo[1.1.1]pentyl-1 chloride and *t*-butyl chloride⁹ suggests that the reaction should be slightly endothermic, and a value of +1 ± 1 has been estimated. The B3LYP and CBS-4 values are in agreement with this estimate.

Finally, the energy of isomerization from the cyclobutyl cation to the cyclopropylcarbinyl cation was estimated. It is known from both calculations¹⁰ and experiments¹¹ that the difference in energy is essentially zero. Most methods give estimated isomerization energies that are in accord with this value.

Conclusions

The MP4/6-31G* and CBS-Q levels of theory were uniformly the more satisfactory methods in reproducing the experimental reaction energies. They are, unfortunately, also the most computationally demanding of the methods. In many cases, MP2/6-31G* gives quite satisfactory results and, except for compounds with acetylenic bonds, B3LYP/6-31G* also gives generally satisfactory results. These two levels of theory are among the

more economical with regard to computer time. In the case of acetylenes, the use of B3LYP/6-311 + G* leads to improved estimates of heats of reaction.

Calculations

All of the calculations were carried out using GAUSSIAN 95.¹²

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